European Polymer Journal, 1970, Vol. 6, pp. 1247–1252. Pergamon Press. Printed in England.

ION-EXCHANGE MEMBRANES PREPARED BY GRAFTING GLYCIDYL ACRYLATE ON PAPER—II

ELECTROPOSITIVE MEMBRANES

E. RIANDE and A. M^{A}. MATEOS
Instituto de Plásticos y Caucho, Patronato "Juan de la Cierva", Madrid

and

G. M. GUZMÁN
Escuela Técnica Superior de Ingenieros Industriales, Tarrasa, Spain

(*Received* 27 *October* 1969)

Abstract—Ion-exchange membranes showing permselectivity have been prepared from parchmentized paper by means of a grafting reaction between the cellulose substrate and a monomer mixture of methyl acrylate and glycidyl acrylate using the ceric ion initiation method. Ionic positive fixed groups have been introduced by reaction with diethylamine followed by quaternization with butyl bromide. Membrane properties have been studied; the influence of reaction conditions upon electrochemical behaviour has been examined. The results show that these membranes have good ion selectivity and are suitable for ion separation processes.

INTRODUCTION

ION-EXCHANGE membranes showing permselectivity may be classified in three groups:⁽¹⁾ homogeneous, where the whole material is of an ion-exchange character; heterogeneous, where the ion-exchange groups are incorporated into the inert matrix by physical mixture or chemical reaction and finally, interpolymer membranes, which are prepared by physical combination of a polyelectrolyte and an inert substrate, both soluble in the same solvent and for which films can be cast from solutions.

A previous paper⁽²⁾ gave descriptions of the preparation and electrochemical properties of grafted glycidyl acrylate–cellulose membranes with electronegative groups. In this paper, a similar topic is presented but the ionic groups introduced into the graft copolymer are of electropositive character.

EXPERIMENTAL

Grafting reactions

Parchmentized paper of density 84 g/m^2 was employed. The sheets were pretreated with 5 per cent NaOH solution at room temperature for 45 min. The grafting reaction was carried out according to the procedure previously described.⁽²⁾ The initially nonporous paper sheet swells in the presence of the NaOH solution. It is likely that some oxidative degradation takes place and low mol. wt. celluloses may be extracted giving rise to pore formation. In addition, there is uncontrolled formation of little vacuoles, which reduce in size once the sheet has been grafted, but which may give rise to unequal distribution of water throughout the cellulose phase.

Opening of the epoxi groups

The grafted sheets were placed in a 10 per cent (v/v) solution of diethylamine in dimethylformamide and kept at 50° for 48 hr. Determination of the introduced amino groups was carried out by washing the sheets with distilled water and then placing them in contact with 1 M HCl solution. The sheets were washed again using distilled water until no acid reaction was shown by the washings, and then were placed in 1 M $NaNO_3$ solution, titrating afterwards the chloride ions liberated (equivalent to the initially introduced amino groups) by means of 0·1 N silver nitrate solution.

Once the amino groups were chemically formed in the grafted substrate, a quaternization reaction was carried out by means of a 50 per cent (v/v) butyl bromide solution in dimethylformamide at 50°.

Membrane properties

Free ion diffusion measurements were performed using a cell similar to that previously described.(2) The sheets were placed between distilled water and 1·5 per cent solution of NaCl. Ohmic resistances were measured at 30° using 0·1 M NaCl solution, platinum electrodes coated with platinum black and a bridge operating at 1000 cps. Membrane potentials were measured by means of a precision potentiometer (Croydon). Calomel electrodes were used and the sheets were previously equilibrated in the more concentrated solution. The electrodes used in measurements were practically symmetric (deviations not larger than 0·1 mV).

It is difficult to obtain the conductance of membranes of low resistance, as that follows from the difference in resistance between the solution with and without membrane. In our case, the membranes were fairly porous and in spite of the electrodes being very close, the resistance of the NaCl solution used was near that of the system membrane–solution. The error of measurement in these cases is higher than that with membranes of low conductance.

RESULTS AND DISCUSSION

One of the methods commonly employed for grafting polymers to a cellulose substrate, without degradation, is oxidation by ceric ions.(3) In a previous paper, this method was applied to the preparation of grafted cellulose membranes made by reaction of a monomer mixture of methyl acrylate with glycidyl acrylate and a cellulose substrate. The first monomer has the effect of decreasing the swelling of the membranes in water; in this sense, its effect is similar to that resulting from a cross-linking agent.

Table 1 shows the relationship of per cent graft to the initial composition of monomer mixture. Per cent graft is defined as:

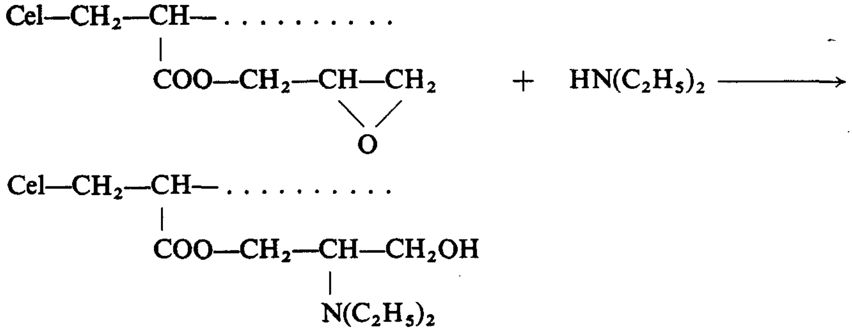
$$\%\ \text{Graft} = \frac{w_g - w}{w} 100$$

where *wg* is the weight of the grafted paper and *w* that of the non-grafted paper.

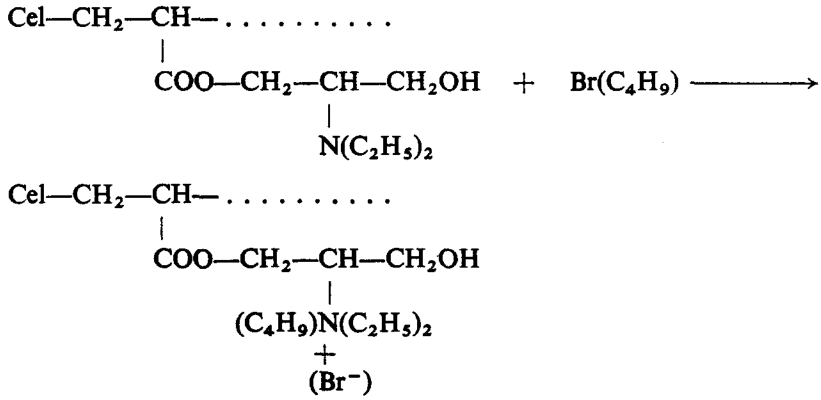
TABLE 1. INFLUENCE OF MONOMER RATIO

Membrane	GA/MA	% Graft
B-2	25/75	440
B-3	40/60	434
B-4	60/40	418
B-5	75/25	395
B-6	100/0	314

The formation of amino groups takes place in DMF. As these groups are hydrophilic, the reaction is likely to be favoured by the presence of water, but the basic nature of the system might promote hydrolysis of the epoxy groups, as shown by Iwakura *et al.*(4) The opening of the epoxy groups can be formulated thus:



Quaternization:



$$\mathrm{Cel{-}CH_2{-}\underset{\substack{|\\ COO{-}CH_2{-}\underset{\substack{|\\ N(C_2H_5)_2}}{CH}{-}CH_2OH}}{CH}{-}\ldots\ldots} + \mathrm{Br(C_4H_9)} \longrightarrow$$

$$\mathrm{Cel{-}CH_2{-}\underset{\substack{|\\ COO{-}CH_2{-}\underset{\substack{|\\ (C_4H_9)N(C_2H_5)_2\\ +\\ (Br^-)}}{CH}{-}CH_2OH}}{CH}{-}\ldots\ldots}$$

Table 2 shows the change in the amount of amino groups produced with time of reaction. Data refer to sheets grafted with a ratio GA/MA = 60/40, a ratio of monomer to water 8/10 (v/v); the per cent graft of these sheets was 310 per cent.

TABLE 2. CHANGE WITH TIME OF THE CONTENT OF AMINO GROUPS

Time (hr)	Millimole of amino groups per gram of dry membrane
2	0·37
4	1·15
6	1·30
24	1·79
72	2·02
120	2·14

The reaction starts rapidly but then proceeds slowly. After 72 hr, the optimum reaction time is reached.

Membranes quaternized by butyl bromide swell in water without losing mechanical strength, with the exception of membrane B–6 (not containing any methyl acrylate).

These membranes show a very rapid ion exchange, probably due to the essentially hydrophilic character of the substrate. For the same reason, their water content changes only gradually and not drastically with the ion exchange capacity, as happens in the case of hydrophobic membranes. Table 3 shows the water content and exchange capacity for different membranes. The per cent water content is defined thus:

$$\% \text{ w.c.} = \frac{w_w - w}{w_w} 100$$

where w_w means the weight of the wet membrane and w that of the dry membrane. Values given in Table 3 for per cent w.c. are only approximate on account of the lack of precision in the method commonly employed for its determination (Ref. 5).

TABLE 3. WATER CONTENT AND EXCHANGE CAPACITY

Membrane	Water content (%)	Exchange capacity m-equiv./g wet membrane
B–2	43	0·55
B–3	58	0·71
B–4	50	0·98
B–5	58	1·04

It can be seen that the variation of water content is less than 35 per cent for membranes B–2 to B–5 while the variation in exchange capacity is much greater (89 per cent).

The selectivity of the membranes depends on the exchange capacity but above all on the distribution of the fixed charges within the membrane. The grafting reactions are carried out on mercerized paper so that the reacting monomers diffuse more easily into the matrix. It can be assumed that the attack of ceric ions is equally probable at any point within the cellulose matrix, so that a uniform distribution of epoxy groups in the interior of the membrane can be expected; the same will happen with respect to the fixed ionic groups, as the opening reaction is carried out in DMF as solvent. On the other hand, the existence of the little vacuoles and the eventually unequal distribution of water in the membrane introduces some uncertainty as to the possible uniformity of its ion exchange properties. For this reason, it is not simple to relate, for instance, the water content to the ratio GA/MA, which is difficult to determine in the interior of the membrane. What can be said with certainty is that once the ionic groups are introduced into the cellulose matrix, the larger the amount of water in the membrane the greater are the existing pores and this reduces the selectivity.

Table 4 indicates the membrane potentials at different ionic concentrations of KCl. For ionic concentrations less than 0·15 M, the selectivity of the membranes approaches that of the ideal case, as shown by the potentials of Table 4. At larger ionic concentrations, the selectivity changes in the same direction as the ion exchange capacity, except for membrane B–3 which is the least selective and has a water content higher than expected (cf. Table 3); the degree of swelling of this membrane would be the largest and so would the pore size. As a consequence, the fixed charges attached to the pore walls of the substrate are less effective in the blockage of ions of the same sign

TABLE 4. MEMBRANE POTENTIALS

c_1/c_2, KCl (mol/l)	E (theor.) (mV)	B–2 (E, mV)	B–3 (E, mV)	B–4 (E, mV)	B–5 (E, mV)
2·0/1·0	−17·0	−8·92	—	—	−6·17
1·0/0·5	−16·2	−10·44	−7·80	—	−9·89
0·6/0·3	−15·7	−12·06	−10·24	−11·40	−11·40
0·3/0·15	−15·7	−13·68	−12·50	−13·57	−13·26
0·15/0·075	−15·8	−14·80	−14·30	−14·67	−14·69
0·05/0·025	−16·3	−15·87	−15·67	−15·88	−15·81
0·025/0·0125	−16·3	−16·12	−16·02	−16·07	−16·20

(the exchange capacity of B–3 with respect to B–2 changes by 29 per cent, while the water content increases by 35 per cent; membrane B–4 increases its exchange capacity by 78 per cent and the water content by 16 per cent, while membrane B–5 increases its exchange capacity by 89 per cent and the water content by 35 per cent). For concentrations of ions in the external solution greater than 0·3 M, the membrane potentials deviate considerably from the ideal values.

Transference numbers can be evaluated approximately by the relation

$$E/E_{max} = 2t_- - 1$$

and this leads to a relationship between transference numbers and ion concentrations. For concentrations below about 0·05 M, the membranes behave as ideally selective. The ionic nature of the $[\overset{+}{N}(R)_3]$ groups inserted into the copolymer matrix is stronger than that of the SO_3^- groups (corresponding to the electronegative membranes of part I(2)). The degree of swelling of the membranes is larger and the selectivity smaller than in the previous case (the selectivity depends both on the pore size and the amount of fixed charges on the pore walls, increasing as the first decreases and the second increases).

Table 5 shows the conductances and ohmic resistances of several membranes. Conductivities are given as $L = 1/RA$, R being the resistance and A the surface of the membrane, and $RA = \rho l$, where ρ is the specific resistance and l the thickness of the membrane.

TABLE 5. CONDUCTIVITY AND OHMIC RESISTANCE

Membrane	Conductivity ($m\Omega^{-1}$ cm^{-2})	Resistance (Ωcm^2)
B–2	90·9	11·0
B–3	158·7	6·3
B–4	110·0	9·1
B–5	133·0	7·5

The order of membranes B–2, B–4 and B–5 is the same as shown in selectivity and exchange capacity, except for membrane B–3 which has an unexpected water uptake.

The free ion diffusion experiments showed values of the order about 1·3–1·6 × 10^{-6} m-equiv./cm^2 sec.

REFERENCES

(1) J. R. Wilson, ed. *Demineralization by electrodialysis.* Butterworths, London (1960).
(2) E. Riande, A. Mª. Mateos and G. M. Guzmán, *Europ. Polym. J.* **6**, 437 (1970).
(3) G. Mino S. and Kaizerman, *J. Polym. Sci.* **31**, 242 (1959).
(4) Y. Iwakura, T. Kurosaki and N. Nakabayashi, *Makromolek. Chem.* **44/46**, 570 (1961).
(5) G. M. Guzmán and E. Riande, *J. Polym. Sci.* **C22**, 887 (1969).

Résumé—On a préparé des membranes échangeuses d'ions semi-perméables à partir de papier parcheminé en utilisant une réaction de greffage entre le substrat cellulosique et un mélange de monomères, acrylate de méthyle et acrylate de glycidyle, l'amorçage étant réalisé par des ions cériques. Des groupements ioniques positifs ont été introduits en faisant réagir la diéthylamine puis en quaternarisant par le bromure de butyle. Les propriétés de cette membrane ont été étudiées; on a examiné l'influence des conditions réactionnelles sur le comportement électrochimique. Les résultats indiquent que ces membranes possèdent une bonne sélectivité vis-à-vis des ions et sont susceptibles d'être utilisées pour leur séparation.

Sommario—Si sono preparate delle membrane per scambio di ioni, con carta pergamenizzata a mezzo di reazione d'innesto tra il sostrato cellulosico e una miscela di monomeri, come acrilato di metile e acrilato di glicidile, facendo impiego del metodo d'iniziazione a ioni cerici. Mediante reazione con dietilammina e facendo seguire la quaternizzazione con bromuro di butile, si sono introdotti dei gruppi fissi ionico-positivi. Si sono studiate le proprietà di tali membrane, come pure se ne è esaminata l'influenza di condizioni di reazione sul comportamento chimico. I risultati mostrano che tali membrane posseggono un'ottima selettività ionica e si prestano per procedimenti di separazione di ioni.

Zusammenfassung—Ionenaustauschermembranen mit selektiver Durchlässigkeit wurden hergestellt aus Pergamentpapier durch eine Pfropfreaktion zwischen dem Cellulosesubstrat und einer Monomermischung von Methylacrylat und Glycidylacrylat nach der Methode der Cer-Ionen Initiation. Gebundene ionische positive Gruppen wurden eingeführt durch Reaktion mit Diäthylamin und nachfolgende Quaternisierung mit Butylbromid. Die Membraneigenschaften wurden untersucht; der Einfluß der Reaktionsbedingungen auf das elektrochemische Verhalten wurde geprüft. Die Ergebnisse zeigen, daß diese Membranen gute Ionenselektivität besitzen und sich zur Ionentrennung eignen.